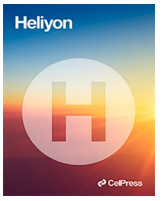
Heliyon 10 (2024) e25515

Contents lists available at ScienceDirect

Heliyon

journal homepage: www.cell.com/heliyon



Review article

Research progress of metal biomaterials with potential applications as cardiovascular stents and their surface treatment methods to improve biocompatibility

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ARTICLE INFO

Keywords:
Cardiovascular diseases
Metal biomaterials
Biocompatibility
Surface treatment
Coating

ABSTRACT

Facing the growing issue of cardiovascular diseases, metallic materials with higher tensile strength and fatigue resistance play an important role in treating diseases. This review lists the advantages and drawbacks of commonly used medical metallic materials for vascular stents. To avoid post-procedural threats such as thrombosis and in-stent restenosis, surface treatments, and coating methods have been used to further improve the biocompatibility of these materials. Surface treatments including laser, plasma treatment, polishing, oxidization, and fluorination can improve biocompatibility by modifying the surface charges, surface morphology, and surface properties of the material. Coating methods based on polymer coatings, carbon-based coatings, and drug-functional coatings can regulate the surface properties, and also serve as an effective barrier to the interaction of metallic biomaterial surfaces with biomolecules, which can be used to improve corrosion resistance and stability, as well as improve their biocompatibility. Biocompatibility serves as the most fundamental property of cardiovascular stents, and maintaining the excellent and stable biocompatibility of cardiovascular stent surfaces is a current research bottleneck. Few reviews have been published on metallic biomaterials as cardiovascular stents and their surface treatments. For the purpose of advancing research on cardiovascular stents, common metal biomaterials, surface treatment methods, and coating methods to improve biocompatibility and comprehensive properties of the materials are described in this review. Finally, we suggest future directions for stent development, including continuously improving the durability and stability of permanent stents, accelerating the development of biodegradable stents, and strengthening feedback to improve the safety and reliability of cardiovascular stents.

1. Introduction

Cardiovascular diseases (CVD) seriously threaten human life worldwide, resulting in high morbidity, disability and mortality rates

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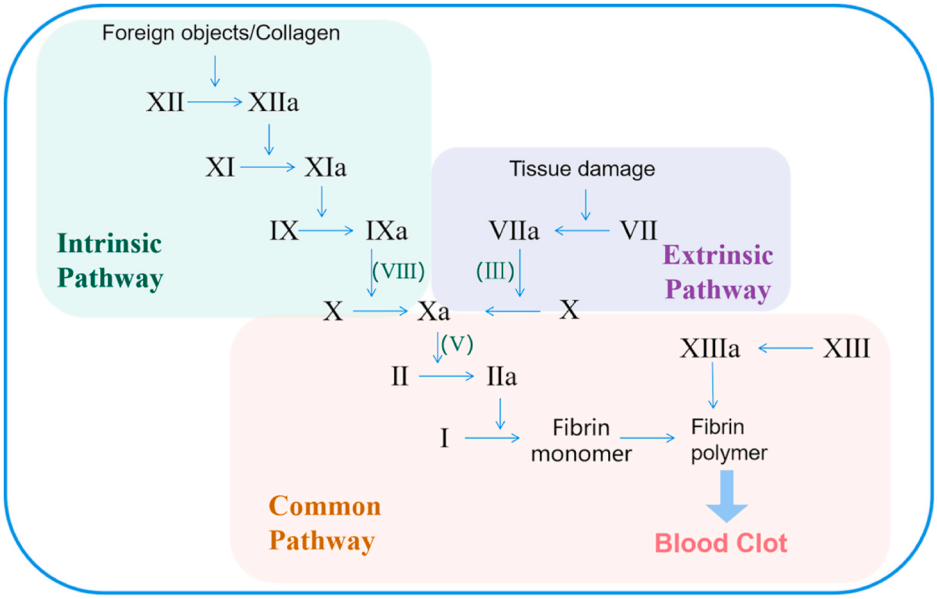
https://doi.org/10.1016/j.heliyon.2024.e25515
Received 26 October 2023; Received in revised form 23 January 2024; Accepted 29 January 2024
Available online 7 February 2024

[1]. Cardiovascular diseases include myocardial infarction, coronary heart disease, heart failure, hypertension, stroke, pulmonary heart disease, rheumatic heart disease, congenital heart disease, atrial fibrillation, and intracerebral hemorrhage. Globally, the number of deaths from cardiovascular disease is enormous, with a significant number of people becoming disabled, according to data reported by the Journal of the American College of Cardiology in 2022 [2]. Consequently, the threat and societal burden of cardiovascular diseases have attracted global attention.

Drug therapy, surgery, and interventional therapy are the three basic forms of treatment for cardiovascular disease. Surgery and interventional therapy can implant dilated cardiovascular stents at the lesion site to restore stable blood supply to the vessels, offering the advantages of good treatment effects and low treatment costs [3]. However, once biomaterials are implanted in the body, interactions occur between the host immune system and the implanted biomaterials, resulting in particular cellular and tissue reactions [4]. Specifically, when blood comes into contact with the implant, the body's defense responses mediated by the activation of cascade reactions in the blood will be triggered, as shown in Fig. 1. Complications arising from this activation may occur, such as allergic reactions, pulmonary and renal dysfunction, thrombosis, and thromboembolism [5]. Clotting can be activated by a complex enzyme cascade that contains an extrinsic pathway and intrinsic pathway, both of which share a common pathway segment at the end. The initiation of both pathways can lead to the activation of X (autoprothrombin C, Stuart factor), resulting in the formation of a fibrin clot. The intrinsic pathway occupies a major portion of the coagulation process. Following vascular injury or the disruption of vascular endothelial integrity, factor XII will be activated to XIIa, factor XIIa will activate factor XI to XIa, and immediately factor IX will become activated to IXa [6], with activated factor IXa attaching to its cofactor (VIIIa) to activate factor X to Xa [7]. When a vessel is traumatized, the extrinsic pathway will be triggered, releasing tissue factor (TF), and TF will bind to factor VII to form a complex that activates factor X. Factor X serves as the first coagulation factor of the common pathway, with factor Xa binding to factor Va to form a complex that activates prothrombinogen (II) to thrombin (IIa). The activation of thrombin drives the translation of soluble fibrinogen (I) into insoluble fibrin (Ia), forming fibrin polymer that serves as scaffolding for clots [8].

Currently, the biggest challenge with cardiovascular stents is the formation of subacute thrombosis and the occurrence of in-stent restenosis after surgery. In clinical practice, patients must still take some anticoagulants and anti-immune drugs after surgery, which may increase the risk of postoperative bleeding [9]. An alternative approach involves focusing on surgical devices and vascular implant materials. The key feature of any material used in cardiovascular medical devices is good biocompatibility, especially good anticoagulant properties, allowing a material to remain relatively stable in the body and resistant rejection and destruction by the host



I	Fibrinogen	VIII	Antihemophilic factor
II	Prothrombin	IX	Plasma thromboplastin componet
III	Thromboplastin, tissue factor	X	Autoprothrombin C, Stuart factor
IV	Ca^{2+}	XI	Plasma thromboplastin antecedent
V	Proaccelerin	XII	Contact factor, Hageman factor
VII	Proconvertin,stable factor	XIII	Fibrin-stabilizing factor

Fig. 1. Coagulation cascade mechanism.

system during the dynamic changes [10]. However, due to the complexity of the human body, the biocompatibility of stents can manifest in many aspects. Stents must not only be stable, anticoagulant, and antiproliferative, but must also be effective in avoiding the delayed healing of endothelial damage caused by antiproliferative drugs. The properties of material surfaces to suppress platelet adhesion and support endothelialization also serve as important targets of biocompatibility [9]. A good balance of other properties for cardiovascular stent materials is also essential, including excellent mechanical properties (i.e., strength, fatigue resistance, and abrasion resistance), corrosion resistance, suitable hydrophilicity, and good antimicrobial properties. Considering these properties, various metal materials with potential application as cardiovascular stents have been researched, with this review focusing on one section.

Compared to ceramics and polymers, metallic implants have sufficient strength and excellent mechanical properties to not only withstand various microfabrication processes, but also support preparation as expandable stents, making surgical treatment less invasive. Stainless steel and titanium alloys exhibit satisfactory physical properties and excellent corrosion resistance, while nickel-titanium alloys exhibit outstanding properties of super-elasticity and shape memory effect. Meanwhile, magnesium, iron, and zinc possess good biocompatibility and biodegradability, and can be used to prepare bioabsorbable cardiovascular scaffolds with fewer long-term effects on the human body. Metal biomaterials serve as a satisfactory material for the preparation of cardiovascular stents due to their varied types and wide property range, which can provide unique properties required for stents. In most cases, a simple single material will have difficulty exhibiting excellent comprehensive performance, and many modification technologies have been proposed. Typical methods to improve the properties of commonly used metal materials include surface treatments and coating methods. Surface treatments can provide beneficial properties to the native material by changing the microscopic morphology and electrical charge of the material surface through physical and chemical methods, while coating methods use biocompatible components, anticoagulant drugs, as well as antibacterial and anti-inflammatory drugs to create a functional surface. At present, the surface treatment of cardiovascular stents still has certain limitations in achieving versatility. For example, vascular stents mainly apply traditional laser technology. However, the laser treatment of metal materials with high mechanical properties and high melting points can cause problems such as ablation and defects, affecting the therapeutic effect after implantation [11]. Various coating methods exist at this stage, however, these coatings often carry specific properties that cannot be balanced. Therefore, obtaining excellent coatings with a combination of properties remains a current research objective. To improve the clinical performance of cardiovascular stents and progress toward multifunctional stents, these aspects require a more in-depth exploration.

This review provides an overview of various medical biomaterials and highlights metal materials with significant potential for the treatment of cardiovascular diseases as cardiovascular stents (section 2). Methods for optimizing the surface biocompatibility of metal materials were reviewed, including surface treatments and coating methods (section 3). Finally, the limitations of these materials and technologies, as well as future research directions to improve their comprehensive performance, were discussed.

2. Metal biomaterials with the potential application as cardiovascular stents

Metal implants exhibit higher tensile strength and fatigue resistance [12]. As a result, metallic biomaterials have been used as biomedical implants since the 20th century. Although various metals and alloys are available, only a few can meet the requirements needed for use as bio-implants. Commonly reported metallic biomaterials utilized as implants include 316L stainless steel [13–15], titanium and titanium alloys [16–18], magnesium and magnesium alloys [19–21], cobalt and cobalt alloys [22,23] and high entropy alloys [24–26].

2.1. 316L stainless steel

316L stainless steel (316L SS) is one of the most commonly employed medical materials, as it can be easily fabricated and exhibits superior mechanical performance, biocompatibility, corrosion resistance, and machinability, with statistically proven medical efficiency [27]. These advantages support 316L SS for the preparation of cardiovascular stents, heart valve components, orthopedic implants, artificial knees and hip joints, as well as artificial bone materials [28]. However, 316L SS exhibits ferromagnetism, leading to poor visibility under nuclear magnetic resonance imaging. In addition, 316L SS contains high levels of chromium and nickel elements, which cause sensitivity issues and are carcinogenic, resulting in serious response issues such as immunoreactions and inflammation [29,30]. To decrease in-stent restenosis, Li et al. [31] investigated the influence and mechanism of copper-containing 316L SS (316L-Cu SS) stents. The researchers concluded that these 316L-Cu SS stents could suppress inflammation caused by endothelial disorders by blocking inflammatory factors. This result was significant, due to the essential factor of inflammation in smooth muscle cell proliferation, thrombosis, and postoperative restenosis. Ren et al. [32] also performed in vitro blood tests on 316L-Cu SS, and the experimental results showed that the blood experienced complete clotting up to 120 min, which was ~55% longer than simple 316L SS, and accompanied by a lower apoptosis rate than vascular endothelial cells (VECs). This demonstrated the improved survival ability of VECs on 316L-Cu SS. Moreover, the platelets adhered to the surface of 316L-Cu SS and retained their regular morphology, with no deformation or agglomeration. 316L-Cu SS released low levels of copper ions per day and had a low cytotoxicity grade, thus, sufficiently meeting the basic requirements for the cytotoxicity of surgical implant materials.

2.2. Titanium and titanium alloys

Since the 1960s, titanium and titanium alloys have been used as metal biomaterials with a wide range of biomedical treatments, including cardiovascular treatment, orthopedics, dentistry, prostheses, as well as craniofacial and joint replacement surgery. Notably,

titanium and titanium alloys can be used as permanent implants due to their good biocompatibility, excellent corrosion resistance, mechanical integrity, and favorable stability [33]. Titanium and its alloys have been regularly used in biomaterials due to their certain load-bearing capacity, lower stiffness and modulus, and superior corrosion resistance compared to other materials [34]. Titanium can spontaneously generate an extremely stable and non-toxic titanium dioxide passivation layer, separating titanium from surrounding body fluids [12]. Due to its lower bioactivity than ceramic materials, titanium is often classified as a biologically inert material [35]. Spataru et al. [36] obtained a new titanium alloy containing Mo and Si via vacuum arc remelting (VAR), which improved the chemical stability and biocompatibility of the alloy.

Nitinol is a near-equiatomic nickel-titanium alloy [37], with distinctive thermal shape memory, super-elasticity and high damping characteristics, and is commonly employed for medical purposes [38]. Researchers have recently focused on the use of nitinol in cardiovascular equipment, due to its greater reversible deformation compared to other metals [39]. Because of its unique properties, nitinol can be used to manufacture functional stents and placed at the surgical site, using a minimally invasive procedure as possible [40]. However, the corrosion process of nitinol will release nickel ions, which exhibit toxic effects and promote the occurrence of alien reactions, thus, reducing the biocompatibility of devices. Wang et al. [41] used acidic electrolytes to electrolytically polish laser-cut nitinol, eliminating slag and oxides from the surface. The surface morphology of nickel-titanium alloy cardiovascular stents (NACS) before and after electropolishing are shown in Fig. 2A and C, respectively. The schematic diagram of the experimental equipment is shown in Fig. 2B.

The electrolytically polished alloy had a smooth and flat excellent surface, which inhibited the adsorption of opal and platelets, reduced the probability of thrombosis, and effectively suppressed the release of nickel ions as well as lowered poisonous effects.

2.3. Magnesium and magnesium alloys

Magnesium and magnesium alloys are considered ideal biodegradable medical implants [42] and have been extensively studied for vascular and orthopedic applications in recent years [43]. Magnesium alloys are bioresorbable materials that can maintain vascular patency during the course of matrix recovery and safely degrade once their mechanical support is not needed. In biodegradable medical implants, controlling the in-vivo degradation rate and non-toxicity of degradation products remains crucial. Costantino et al. [44] found that Mg-based biomaterials demonstrated excellent cell compatibility on macrophages. This makes these cells critical in the inflammatory process, and allows them to influence the outcome of tissue healing and implant performance, inducing faster inflammation regression and tissue repair.

Mao et al. [45] prepared a magnesium-based alloy (Mg-2.2Nd-0.1Zn-0.4Zr) with a stable degradation rate, along with long-term structural and mechanical durability in vivo. The in vitro cell toxicity of the magnesium extract was assessed by human vascular endothelial cells (HUVECs). As shown in Fig. 3, these cells behaved normally and were healthy with a typical cobblestone morphology, indicating that the corrosion products of the magnesium alloys produced negligible toxic effects. Six months after implantation of the alloyed vascular stent into a rabbit body, angiography analysis indicated good anastomosis between the stent and tube wall, without acute thrombosis or severe in-stent restenosis (ISR). Dvorsky et al. [46] indicated that AM50 magnesium alloy could serve as a potential option for biodegradable stent applications, due to its suitable corrosion rate of 1.2 mm/year and good cellular compatibility.

2.4. Zinc and zinc alloys

Zinc is an indispensable trace element for the growth and development of all living organisms [47]. Zinc-based biomaterials have

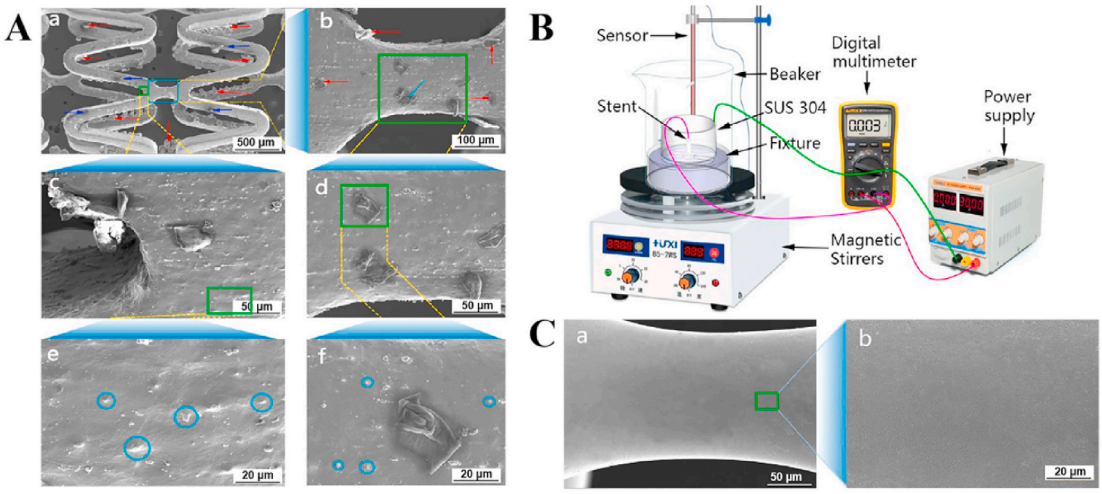


Fig. 2. Surface morphology of NACS before (A) and after (C) electropolishing; schematic diagram of the laboratory device for the electrolytic polishing of NACS (B). Reprinted with permission from Ref. [41]. Copyright 2022 Springer Nature.

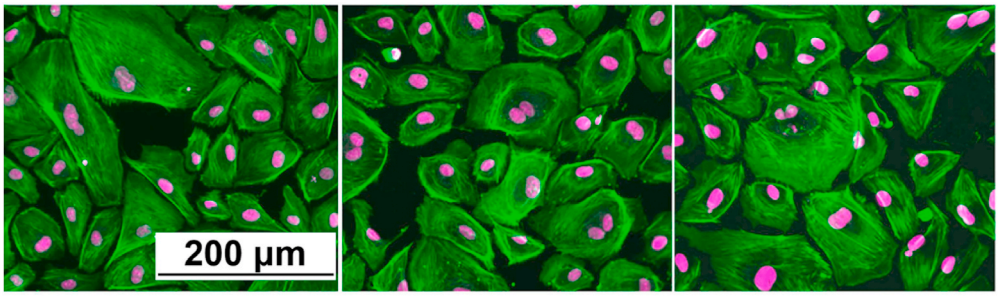


Fig. 3. Morphologies of HUVACs in the negative control and Mg extract with 10% and 50% dilution (left to right) after 24 h. The cells were fixed and stained for cytoskeleton (green) and nuclei (purple). Reprinted with permission from Ref. [45]. Copyright 2017 Springer Nature. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

been used as new degradable metallic biomaterials for orthopedic devices, cardiovascular stents and other medical applications. Unlike other degradable metals (i.e., Mg, Fe), the corrosion process of Zn does not produce hydrogen and has a more moderate corrosion rate [48]. Lin et al. [49] produced a zinc-based material for the novel exploitation of biodegradable cardiovascular stents by adding trace amounts of magnesium and copper. Compared to pure Zn, the Zn-based alloy possessed greater mechanical properties, as well as excellent cytocompatibility and hemocompatibility. The Zn-based stents were successfully implanted into the left carotid arteries of New Zealand white rabbits for up to 12 months. All of the rabbits survived without any adverse clinical events, indicating the low cytotoxicity and thrombosis risk of the Zn-based stent. Fig. 4A shows the hematoxylin-eosin (HE) staining sections of the stented arteries after 1 week, 1, 3, 6, and 12 months after implantation. The neointima area and lumen stenosis rates of the stented segments 1, 3, 6, and 12 months after implantation are shown in Fig. 4B and C, respectively. Immediate endothelialization was

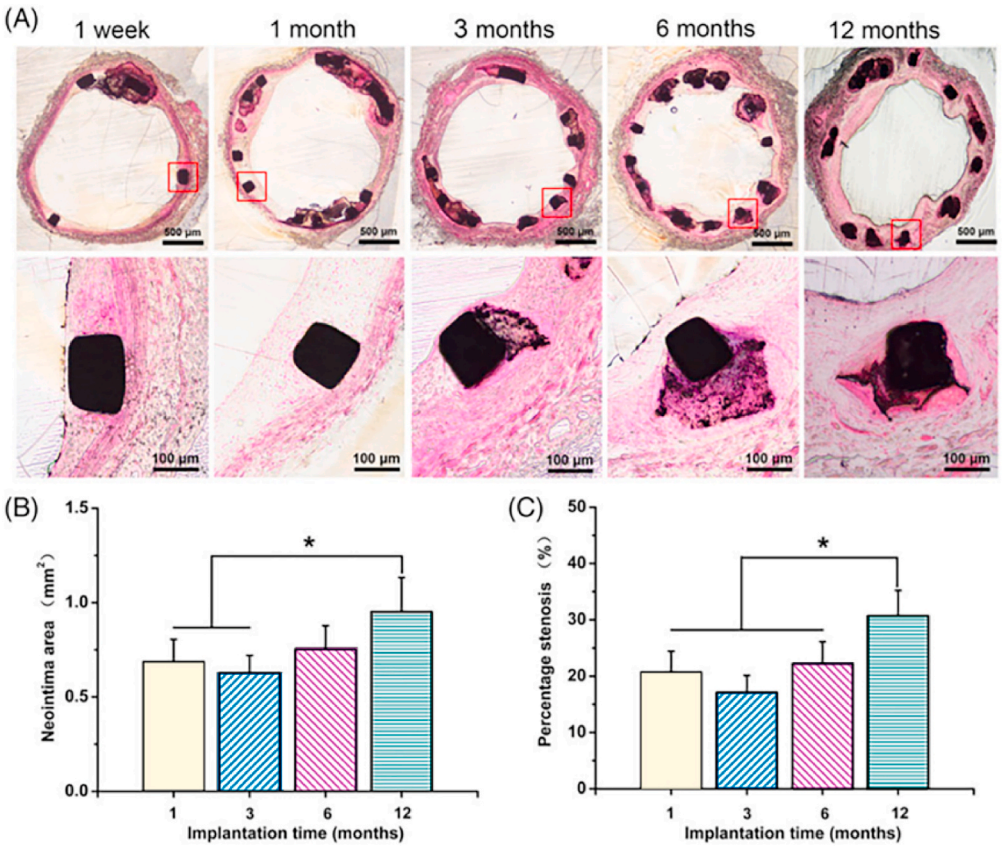


Fig. 4. (A) Hematoxylin-eosin (HE) staining sections of the stented arteries 1 week, and 1, 3, 6, and 12 months after implantation; (B) neointima area; (C) lumen stenosis rates of the stented segments 1, 3, 6, and 12 months after implantation (red boxes mark the magnified areas ($n = 4$, $^*p < 0.05$)). Reprinted with permission from Ref. [49]. Copyright 2018 John Wiley and Sons. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

observed 1 week after implantation, and the results showed that both the neointima area and lumen stenosis rate of the stent increased over time.

To further enhance the hemocompatibility of degradable Zn-based stents and enhance their advantages as cardiovascular stents, Yin et al. [49] designed three Zn-based stents (Zn-0.8Cu, Zn-0.8Mn, and Zn-0.8Li) and conducted comprehensive hemocompatibility experiments with pure zinc and 316L SS stents as comparison groups. It was found that the hemocompatibility of these three Zn alloys was better than that of pure Zn and comparable to that of 316L SS. The hemolysis rate of these three Zn alloys was around 0.5%, which was significantly lower than the judgment standard of 5% set by the ISO 10993-4 standard. The platelets on the surface of pure Zn were activated and formed pseudopods, the platelets on the surface of 316L SS exhibited agglomeration, and no obvious platelet activation or agglomeration was observed on the three types of Zn alloys. These Zn alloys possess excellent anti-thrombotic and anti-platelet adhesion properties and are considered promising vascular stent materials.

2.5. Cobalt and cobalt alloys

Cobalt and cobalt alloys possess excellent antimicrobial properties, with widespread use in a variety of biomedical applications such as dentistry, cardiovascular treatments, and orthopedic devices [50]. Co alloys exhibit favorable corrosion resistance without pitting and crevice corrosion, as these alloys can release Co ions in solutions to stabilize the passive film and Co ions can be repetitively released in the wear situation [51]. Strehblow et al. [52] assessed the clinical response of 199 patients with Arthos Pico stent implants (cobalt-chromium alloy stent) and found that the stent implantation procedure had a 99% success rate, with acute and subacute stent thrombosis rates of 0.5% and 1.5%. The 6 and 12 month post-operative event-free survival rates were 87% and 85%, suggesting that treatments with surgical stent implantation were relatively safe and effective. Wang et al. [53] designed a new cobalt alloy (nickel-free) for the preparation of vascular stents, resulting in excellent mechanical, corrosion resistance, and biological properties. The cobalt-base alloy had non-cytotoxic effects, while the L-929 mouse fibroblasts cultured on the alloy were spindle-shaped and grew well. The new alloy was as safe as the L605 alloy (a conventional stent material), as verified by the measurement of apoptosis (programmed cell death) of the L-929 cells through flow cytometry. Schieber et al. [54] controlled endothelialization and platelet adhesion by modifying the cobalt-chromium (CoCr) alloy surface through direct laser interference patterning (DLIP) with different cycles and depths, as shown in Fig. 5. This served as a promising method for accelerating endothelial recovery and avoiding surface thrombosis in cardiovascular applications.

2.6. High entropy alloys

High entropy alloys (HEAs) are near equimolar alloys containing five or more elements [55], attracting significant interest due to their range of functional properties, including good mechanical properties and biocompatibility [56]. Compared to conventional

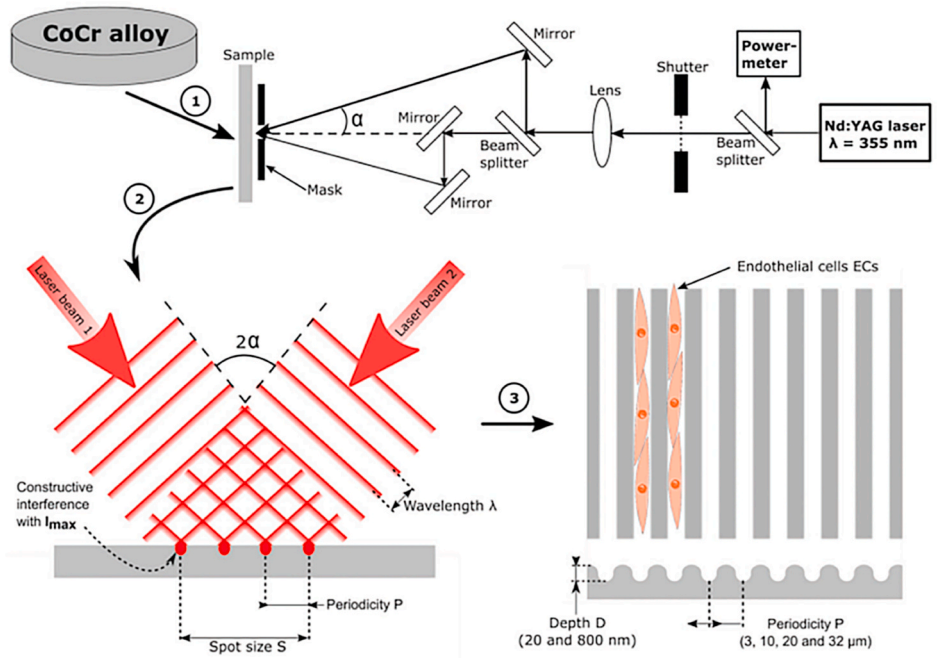


Fig. 5. Steps to produce a patterned CoCr surface by DLIP: (1) configuration of the experimental DLIP setup; (2) interference schematics of the two laser beams on the CoCr planar surface; (3) front- and top-views of the modified CoCr surfaces and simulation of the expected EC adhesion orientation after patterning. Reprinted with permission from Ref. [54]. Copyright 2017 John Wiley and Sons.

medical alloys, HEAs offer better design freedom, integrating medical capabilities to suit diverse medical needs such as a low modulus of elasticity, high biocompatible elements, and potential shape-memory capabilities [57]. Alagarsamy et al. [58] verified the possibility of using an $Al_{0.1}CoCrFeNi$ HEA as a peripheral vascular stent by assessing its mechanical properties and comparing them with commercial 316L SS stent materials. The study found that the high-entropy alloy either approached or outperformed 316L SS in various mechanical properties, exhibiting higher fatigue life, which was beneficial for reducing the failure rate of stent implants. Chen et al. [59] designed a new $Co_{40}Fe_{35}Cr_{16}Ni_8Ti_1$ HEA for coronary stents, which met the mechanical property and corrosion resistance requirements of common coronary stent materials on the market. This alloy exhibited good elongation and its yield strength and tensile strength reached 588 and 932 MPa, respectively, offering novel insights for the development of high-performance coronary stent materials. The $TiHfZrNb_x$ HEA with a high radial strength has shown to be ideal for the preparation of small diameter vascular stents. Tanji et al. [60] concluded that the $TiHfZrNb_x$ HEA exhibited higher corrosion resistance compared to standard CP-Ti and Ti_6Al_4V alloy biomaterials, making it a promising high performance medical implant material.

The advantages and disadvantages of commonly used metal biomaterials are summarized in Table 1. One of the most prominent problems faced by metal materials is the presence of various corrosive substances in blood and body fluids, such as water, amino acids, plasma, assorted ions, and dissolved oxygen. Once implanted inside the body, the metal stent will be electrochemically attacked by these corrosive substances and release metal ions [13], which can spread throughout the body via blood flow and may negatively impact human tissues and partially accumulate in organs, such as the liver, kidneys, and spleen [61]. Some of the released metal ions may even act as powerful allergens and carcinogens. Therefore, metallic stents must be more biocompatible and possess exceptional corrosion resistance in the human body. In addition, there is growing demand for materials that can be utilized to prepare implant devices with superior material-biological interface stability.

3. Methods to improve the biocompatibility of materials

3.1. Surface treatments

Many surface treatment methods currently exist, including chemical methods [68] and physical methods [69]. Physical methods consist of milling [70], laser [71–73], sandblasting [74,75], and electrical discharge machining (EDM) [76,77], while chemical methods include acid [78] and alkali treatment [79,80], nitriding [81,82], and plasma treatment [83,84]. In addition, some electrochemical methods are available, such as electropolishing [85,86], electrolytic polishing [87,88], anodic oxidation [89,90], and micro-arc oxidation (MAO, also known as plasma electrolytic oxidation) [80,91]. These methods can enhance the biocompatibility of the material surface by changing the surface morphology, surface wettability, roughness, surface charge, and functional properties of the surface in different ways to meet the application requirements.

3.1.1. Rotational magnetorheological abrasive flow finishing

The nanoscale surface finish of biomedical implants made of metals such as 316L stainless steel (SS 316L) and titanium alloys is essential for their biocompatibility [11]. Karthikeyan et al. [92] developed a rotational magnetorheological abrasive flow finishing (R-MRAFF) process to finish SS 316L, and the impact of surface roughness on hemocompatibility was assessed by a platelet adhesion experiment. The results showed that the homogeneous nanoscale surface successfully improved hydrophilicity, corrosion resistance,

Table 1
Advantages and disadvantages of commonly used metal biomaterials.

Metal biomaterials	Advantages	Disadvantages	References
316L SS	Low cost Good mechanical properties, biocompatibility, corrosion resistance and machinability	Contain high levels of Cr and Ni which has sensitization and carcinogenicity, causing immunoreactions and inflammatory responses	[28]
Ti and Ti alloys	Good biocompatibility, corrosion resistance, mechanical integrity and stability	Relatively biologically inert surface No antimicrobial properties Poisoning of the body caused by the release of metal ions and their accumulation in the soft tissues of the body.	[62,63]
Mg and Mg alloys	Biodegradable Good mechanical strength and biocompatibility Non-toxic Low thrombogenicity	Rapid degradation Poor ductility	[64]
Zn and Zn alloys	Biodegradable Moderate corrosion rate Adjustable mechanical properties Good biocompatibility Non-toxic	Low mechanical strength	[65,66]
Co and Co alloys	Excellent antimicrobial properties Good mechanical strength and corrosion resistance	Co is toxic to fibroblasts and can trigger inflammatory mediator	[50,51,67]
High entropy alloys	Well-balanced mechanical properties Good biocompatibility High degree of design freedom	Immature preparation process High cost	[56,57]

and biocompatibility of the 316L SS. The R-MRAFF machine setup and epifluorescence micrograph of platelet adhesion on samples with different surface roughnesses are shown in Fig. 6A and B, respectively, indicating that platelet adhesion decreased significantly when the surface roughness decreased from 319 to 167 nm.

3.1.2. Laser surface modification

Laser surface modification (LSM) is a beneficial method for biomaterial processing. Balla et al. [93] demonstrated that laser surface melting served as an effective strategy for tailoring the surface crystallographic texture of 316L SS biomedical devices. The researchers used continuous wave laser to melt the surface of medical 316L SS, and found that the LSM samples with increased planar lattice spacing and high concentration of low-energy grain boundaries exhibited better surface wettability, corrosion resistance, as well as enhanced viability and in vitro cell-material interactions. Zhang et al. [94] demonstrated that laser shock peening (LSP) could serve as a viable surface modification technique for improving the mechanical properties, corrosion resistance, and biocompatibility of NiTi alloys to satisfy the demands of biomedical applications. To evaluate the cytotoxicity, cell adhesion, and spread of the samples before and after LSP, adipose-derived stem cells (ADSCs) were used to perform LIVE/DEAD staining and then seeded and cultured onto the samples. As shown in Fig. 7(1), the average cell survival rates and live cell density were higher on the LSP samples. In addition, the cells grew and spread better on the LSP-treated surface, as shown in Fig. 7(2), which meant that compared to the non-lasered samples, the LSP-treated materials were more cell-friendly and biocompatible.

Oberringer et al. [95] studied the influence of nanostructured patterns prepared by femtosecond laser technology on the surface of 316L SS for stent application. The researchers assayed the cytocompatibility of the prepared surfaces using a co-culture system consisting of normal human dermal fibroblasts (NHDFs) and human dermal microvascular endothelial cells (HDMECs). The results showed a significant reduction in myofibroblast proliferation on the laser-treated samples compared to the untreated samples. Laser femtosecond technology could modulate the stent surface morphology of the metal substrate to prevent or reduce restenosis.

3.1.3. Electric discharge machining

The electric discharge machining (EDM) process is valuable for designing bioimplant materials and can improve the morphology conducive to cell ingrowth. This technology can generate a controlled high-frequency electric spark between the tool electrode and workpiece after creating an ionized zone in the medium, causing metallurgical transformation by increasing the temperature in the specimen area [96]. Without physical contact between the tool and the work surface, mechanical forces may be completely negligible [97]. EDM can cut difficult-to-machine high-temperature alloys such as titanium-based [97] and nickel-based alloys [98] with a guaranteed surface finish. Mahajan et al. [96] treated the surface of a Co–Cr alloy to investigate the surface performance and biological responses. The researchers observed that the EDM-treated samples exhibited improved blood interaction biocompatibility, and hemocompatibility. Mahajan et al. [99] performed EDM on the surfaces of commercially available biomaterial substrates (Co–Cr alloy (F90), β-Ti, and 316L SS) and investigated their in vitro biocompatibility, corrosion, and tribological properties. The researchers found that discharge treatment increased the corrosion resistance of cobalt-chromium, titanium, and stainless-steel alloys by 86.39%, 62.15%, and 56.21%, respectively. The surface of the discharge-treated samples exhibited good blood flow compatibility, and no highly hemolyzed, aggregated, or deformed red blood cells were observed on the untreated samples. These results verified the effective application of EDM in the biomedical field.

3.1.4. Plasma treatment

The surface cleaning and sterilization of biomaterials are crucial steps before they can be implanted. Material surface cleaning is a vital component of the surface treatment process [100], and plasma treatment can be used to complete this task. Plasma serves as the fourth state of matter, consisting of a partially or fully ionized gas composed of electrons, ions, free radicals, and neutrals [101]. Plasma biology is a new interdisciplinary research field, allowing for the introduction of other functional groups such as hydroxyl, amino, and carboxyl groups onto the surface of biomaterials to enhance their biocompatibility. Plasma surface modification is considered a

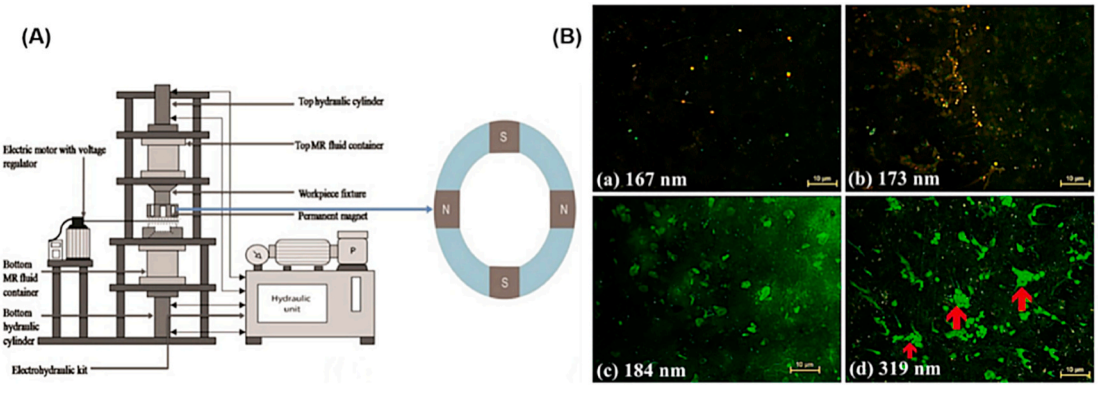


Fig. 6. (A) R-MRAFF setup and (B) epifluorescence micrograph of platelet adhesion on samples with different surface roughnesses. Reprinted with permission from Ref. [92]. Copyright 2021 Elsevier.

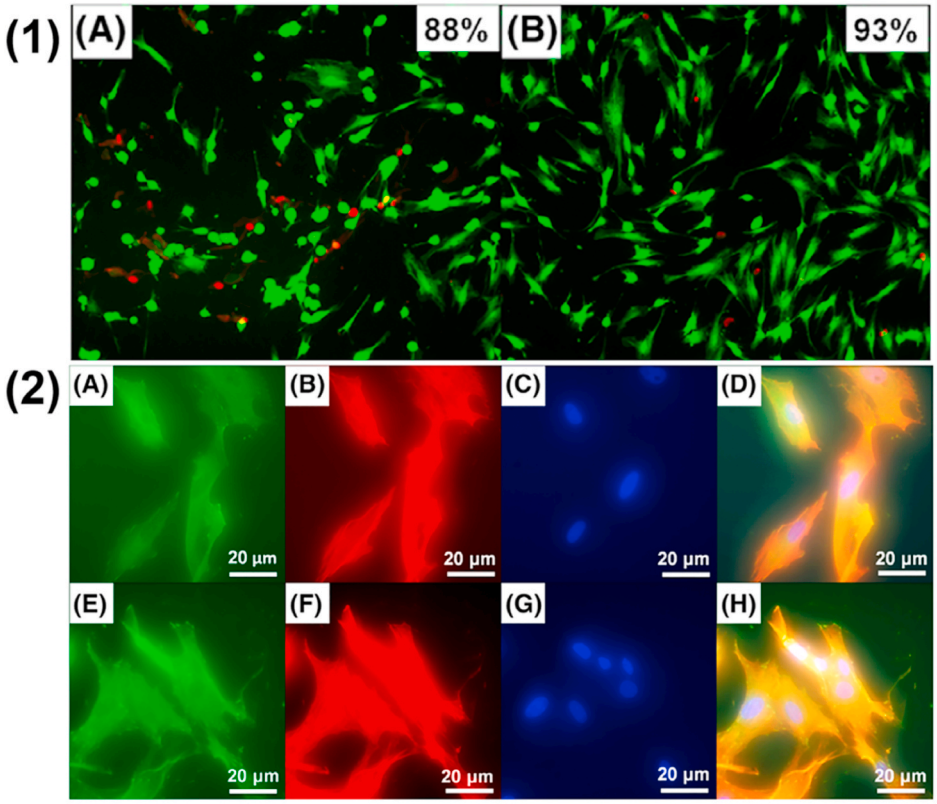


Fig. 7. (1) LIVE/DEAD staining of the ADSCs on the (A) untreated sample and (B) LSP-treated sample (ADSCs were incubated on each sample for 24 h, with the dead cells in red and living cells in green); (2) ADSC adhesion patterns on the untreated samples (A–D) and LSP-treated samples (E–H). The ADSCs were incubated on each sample for 48 h, and then focal contacts were labeled with anti-Vinculin (green); the actin cytoskeletons were labeled with TRITC-conjugated Phalloidin (red); and the nulcei were labeled with DAPI (blue). Pseudocolor overlays were used to represent the monochrome pictures. Reprinted with permission from Ref. [94]. Copyright 2018 John Wiley and Sons. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

versatile modification technique in the biomedical industry with the unique advantage of selectively enhancing surface properties without altering the other biomaterial properties [102]. The plasma treatment method is an effective method that can be applied to cardiovascular materials. For example, adopting this method can create a graded barrier layer on NiTi alloy substrates to reduce the diffusion of nickel ions and enhance implant safety [103]. Campeol et al. [104] oxidized F2063 nickel-titanium alloys by plasma treatment to obtain a positively increased open circuit potential in phosphate-buffered saline (PBS), demonstrating that the corrosion resistance was significantly improved. In addition, plasma oxidation increased the super-elasticity of TiNi by 8.6%. This improved corrosion resistance and mechanically-enhanced surface provided TiNi with the capability to prepare self-expandable implants and stents. Ujino et al. [100] suggested that this atmospheric pressure low-temperature plasma treatment could effectively clean the surface of the substrate by ionizing the reactive gas or surrounding atmosphere and generate plasma to collide with the sample surface, separating and volatilizing the carbon bonds in the organic contaminants. Meanwhile, atmospheric pressure low-temperature plasma treatment could introduce hydrophilic groups on the titanium discs, improving the hydrophilicity of titanium to enhance the adhesion of proteins to cells. Jenko et al. [105] proposed a new plasma treatment method by treating TiNi for 10 s with H_2 plasma followed by a mixed plasma of 90% H_2 and 10% O_2. This method reduced the Ni contents on the surface and quickly formed a Ni-free titanium dioxide layer. The plasma-treated samples demonstrated superior corrosion resistance in the simulated physiological Hanks solution, with the breakdown potential expanding from 600 to 1300 mV, while the corrosion current density decreased from 0.3 to 0.06 μA/cm^2, and the corrosion rate decreased from 2.6 to 0.4 μm/year. Correspondingly, the release of Ni was negligible. The plasma-treated TiNi could stimulate the proliferation of activated human cells without any cytotoxic effect on the L929 cells, demonstrating good biocompatibility possessed by the plasma-treated TiNi. Benčina et al. [106] hydrothermally and plasma treated titanium to obtain a surface with a superhydrophilic and bioreactive titanium oxide layer. Through blood compatibility experiments, the researchers observed a homogeneous distribution of platelets in an unactivated state on the treated titanium surface, which indicated a low risk of thrombosis. After additional experiments, the researchers found that this titanium surface supported the adhesion and growth of human coronary artery ECs, while inhibiting human coronary artery smooth muscle cells (SMCs). This phenomenon demonstrated that the plasma-treated titanium not only achieved rapid endothelialization, but also avoided in-stent restenosis. The nitriding and fluorination processes subsequently introduced could also be achieved by plasma treatment [107,108].

3.1.5. Nitriding

Nitriding is a common surface treatment technique that hardens material surfaces to improve wear resistance [109,110] and antibacterial effects [111], and has been applied in medicine. Bédouin et al. [112] treated the surface of a Ti–27Nb alloy by high temperature gas nitriding, which improved the surface hardness and corrosion resistance, endowing it with high chemical stability and enhancing cell viability. Lin et al. [107] nitrided austenitic stainless steel using plasma, which not only enhanced the corrosion resistance and surface hardness of the stainless steel, but also imparted antibacterial properties, thus, increasing the probability that stainless steel could serve as an essential material in biomedical applications.

3.1.6. Fluorination

Fluorination is a common technique or pretreatment used to optimize the degradation kinetic and enhance the biocompatibility of alloy implants [113], which has shown to be suitable for complex structures such as cardiovascular stents [114]. Fluorinated biomaterials have been used to obtain antibacterial activity and cell compatibility, promoting cell proliferation and activation [108]. Zhang et al. [114] designed a novel Mg-Nd-Zn-Zr alloy (JDBM) for cardiovascular stent applications, which was immersed in hydrofluoric acid for fluorination (HF-JDBM). The treated sample possessed increased surface roughness and hydrophilicity, while the MgF_2 layer formed by fluorination could mitigate the degradation rate of JDBM in the first 10 days. Surface fluorination of JDBM could improve the proliferation of HUVECs and no unfavorable effect was observed on HUVEC spreading. The live/dead fluorescent microscopy images and HUVEC spreading morphology are shown in Fig. 8A and B, respectively.

3.1.7. Electrochemical polishing

Electrochemical polishing, also known as electropolishing, is a well-known surface treatment method. Compared to mechanical polishing, electrochemical polishing has unique advantages for vascular stents with specific shapes and designs. Zhao et al. [115] electrochemically polished titanium-nickel alloy stents and found that electrochemical polishing not only maintained the mechanical strength of the stents, but also improved the smoothness, which was important for their biocompatibility. Kityk et al. [116] found that the electrolytic polishing of titanium alloys using ethaline as a deep eutectic solvent not only ensured satisfactory surface flatness, but also allowed for flexible changes in surface wettability by controlling the time and potential, which serve as a key factor in influencing the interactions between the implant and surrounding host tissue, thus, determining the biocompatibility of the material.

3.1.8. Oxidation

Formation of an oxide layer through oxidation serves as an important technique to affect the corrosion behavior of alloys and improve the biocompatibility of materials [39,117,118]. Sullivan et al. [117] adopted five processing methods to change the titanium oxide layer on the nitinol stents and the corresponding photographs are shown in Fig. 9. The researchers found a strong dependency between the oxide layer thickness and accumulated Ni release.

Jo et al. [119] formed an oxide coating on a pure magnesium substrate by anodic oxidation and micro-arc oxidation, which improved the biocompatibility of magnesium and reduced the degradation rate. Zhang et al. [120] fabricated a honeycomb

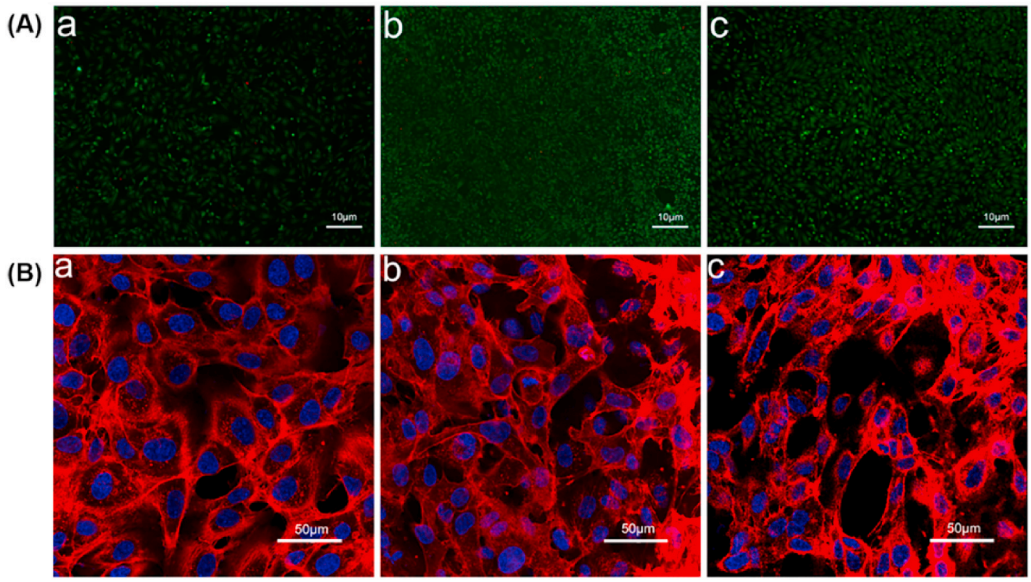


Fig. 8. (A) Live/dead staining results of the HUVECs co-cultured with a) JDBM, b) HF-JDBM disk sample, and c) negative control for 5 days; green emission for live HUVECs and red emission for dead cells; (B) fluorescent microscopy images of the HUVEC cytoskeleton (red emission) and nucleus (blue emission) cultured in 10% extract of a) JDBM, b) HF-JDBM, and c) for negative control. Reprinted with permission from Ref. [114]. Copyright 2013 Springer Nature. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

nanostructure on the surface of pure titanium using two-step anodization and annealing treatment, with the fabrication procedure shown in Fig. 10(a–e). The process of anodic oxidation and annealing treatment at 500 °C effectively enhanced the mechanical strength, corrosion resistance, and hemocompatibility of the titanium substrate. Both in vitro and long-term in vivo experiments indicated that the modified samples significantly inhibited the adhesion of platelets and blood cells and suppressed thrombosis and restenosis formation.

3.2. Coating methods

The coatings can act as effective barriers to hinder interactions between the metal biomaterial surface and biomolecules. Modulating the surface performance of coatings (e.g., morphology, wettability, roughness, crystal structure, element composition, and charges) can eventually lead to improvements in corrosion resistance, mechanical properties, stability, as well as the inhibition of protein uptake and hematopoietic activation [120]. Numerous efforts by researchers have resulted in the development of various coatings with particular functions for diverse metal biomaterials, such as carbon-based coatings [121,122], polymer coatings [123–125], drug-functional coatings [126–128], and biofunctional coatings [129,130]. The biological coating materials applied to the cardiovascular stents were bound to directly contact human tissue fluids, blood, tissue, and cells, making the high requirements of biocompatibility and non-toxicity necessary.

3.2.1. Carbon-based coatings

Carbon-based materials such as carbon nanotubes and graphene are considered promising candidates for biomedical applications. Specifically, graphene is considered a fundamental building block for carbonaceous materials with different dimensions (Fig. 11) [131]. As a result, graphene and its derivatives have attracted interest from many researchers in the field of biomedical applications due to their high mechanical strength and good biocompatibility [132]. Wawrzyńska et al. [133] coated graphene on the surface of a 316L substrate to enhance its biocompatibility and blood compatibility, and reduce in-stent restenosis and thrombosis.

Diamond-like carbon (DLC) provides high biocompatibility and biocidal reaction, and has become a suitable approach in orthopedics, cardiovascular, and dental applications. DLC coatings have high hardness, good insulation, wear resistance, chemical stability, and biocompatibility [134]. Hang et al. [135] fabricated DLC coatings on NiTi alloys using arc-enhanced magnetron sputtering. The adhesion, morphology, and viability of endothelial cells (ECs) on the DLC coatings were better than those on bare NiTi alloy, suggesting that surface-modified NiTi alloys with DLC coatings could serve as promising materials for cardiovascular applications.

3.2.2. Polymer coatings

Diverse chemical compositions offer many physicochemical properties in polymers, allowing them to be widely utilized in biomedicine [136]. The surface functional groups and structure of polymers can modulate the surface hydrophobicity, non-specific protein adsorption, stability of biomaterials, and antifouling properties. However, compared to metallic and ceramic materials, polymer-based materials have limited mechanical properties and can barely be directly used in an unmodified state [136]. Anil et al. [137] developed two polymer coatings consisting of polycaprolactone (PCL) and poly-ω-pentavalerolactone (PPDL) on a magnesium surface, to address the issue of magnesium rapidly disintegrating in vivo and enhancing its potential application as a cardiovascular stent. The results showed that the polymer coatings notably strengthened the corrosion resistance of magnesium and the corrosion resistance increased with polymer coating thickness. Additionally, in vitro cytotoxicity testing was performed according to ISO10993-5. The results indicated that the uncoated magnesium substrate had a cell survival rate of 20–30%, while the polymer-coated substrate possessed a cell survival rate of 70–85%. These two polyester coatings effectively improved the corrosion

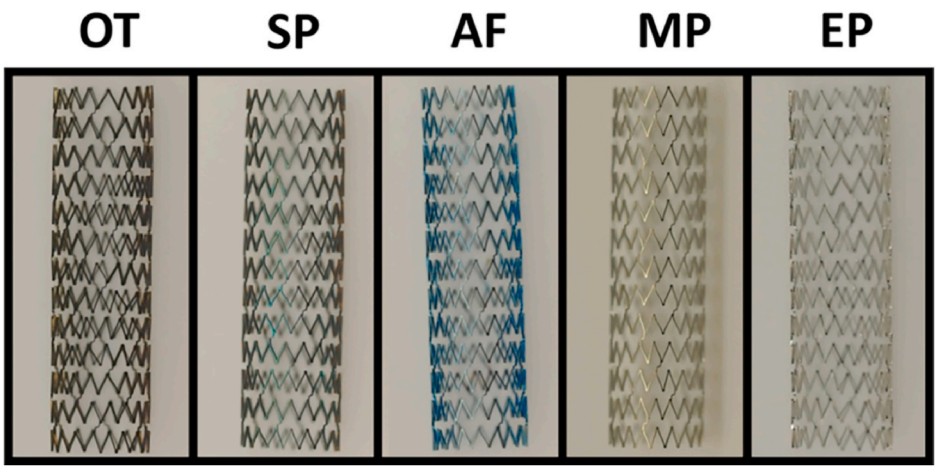


Fig. 9. Photographs of stents fabricated using the following surface treatments: oxidized tube (OT), air furnace (AF), salt pot (SP), mechanical polishing (MP), and electropolishing (EP). Reprinted with permission from Ref. [117]. Copyright 2015 Springer Nature.

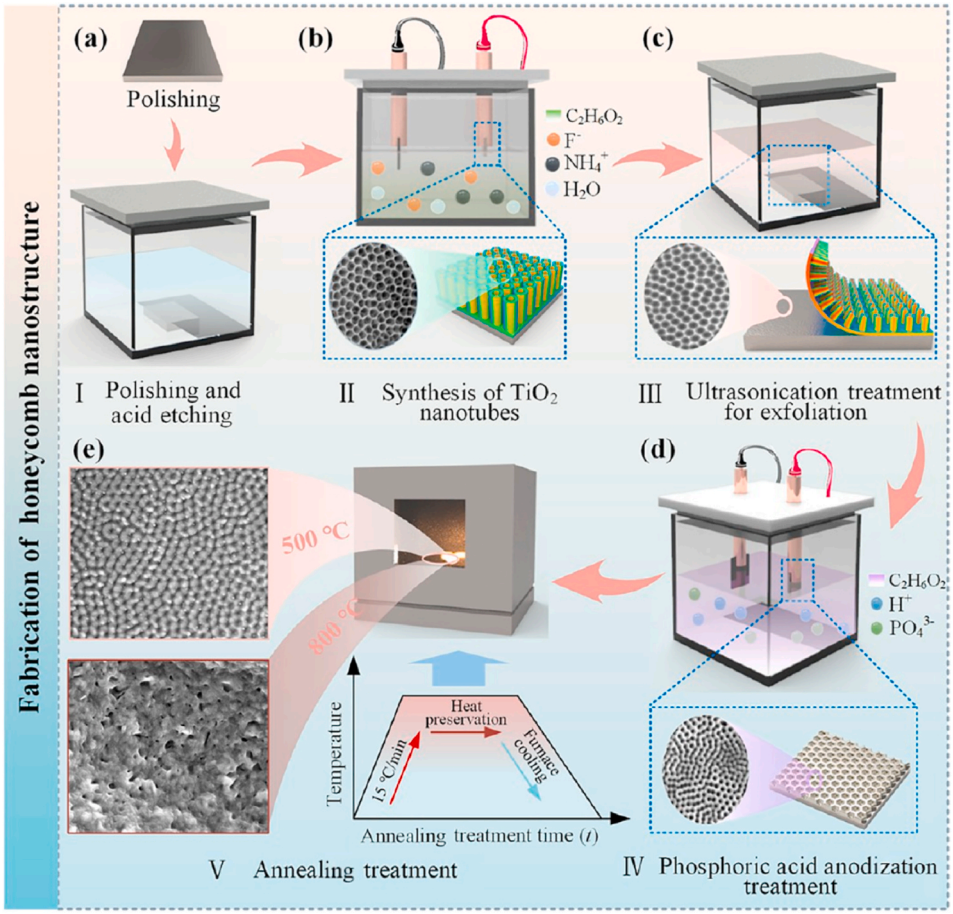


Fig. 10. Preparation process of the honeycomb nanostructure; (a) polishing and acid etching of the Ti substrate; (b) synthesis of TiO_2 nanotubes; (c) ultrasonic treatment for exfoliation of the nanotube layer; (d) synthesis of the honeycomb nanostructure; (e) diagram of annealing treatment for the honeycomb nanostructure. Reprinted with permission from Ref. [120]. Copyright 2022 American Chemical Society.

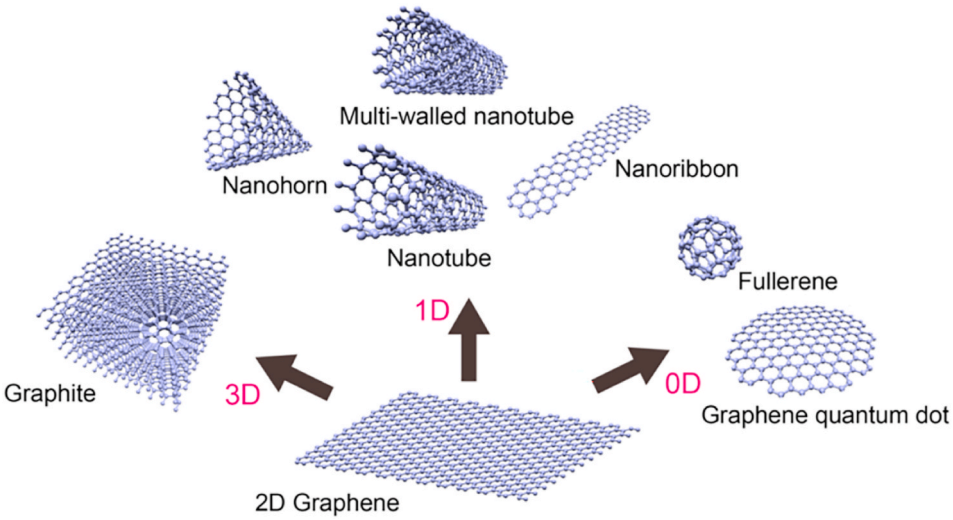


Fig. 11. Carbonaceous materials with different dimensions. Reprinted with permission from Ref. [131]. Copyright 2018 Taylor and Francis Ltd.

resistance of magnesium, decreased the release of metal ions from the rapid degradation of magnesium, and increased its biocompatibility. Li et al. [138] used plasma to apply polymer coatings to the surfaces of medical NiTi alloys to increase their hemocompatibility. The study discovered that NiTi with a 2,2,3,4,4,4-hexafluorobutyl methacrylate (PHFMA) coating had a higher corrosion potential than NiTi, because the PHFMA coating acted as a barrier layer to reduce charge exchange and electron transport on the surface. The platelet adhesion assay results showed that the number of platelets on the PHFMA coated surface was significantly lower. The PHFMA coating could serve as an effective means of preparing the blood compatible surfaces of alloys for cardiovascular applications.

Conductive polymers typically have backbones with alternating single and double (or triple) covalent bonds [139], and can combine both electronic and ionic conductivity as well as possess biocompatible interfacial properties [140]. Polypyrrole (Ppy) is a conductive polymer with the characteristics of easy synthesis, high electrical conductivity [141], and good biocompatibility, exhibiting favorable environmental stability and cell adhesion through various cell growth processes [142]. Additionally, Ppy is crucial for biomedical applications, drug delivery, tissue engineering, bioactuators, and biosensors. However, Ppy has the disadvantages of brittleness, low strength, and difficult post-synthesis processing. Ppy coatings have shown poor adhesion to oxidizable metals, and one potential strategy to resolve this issue involves doping them with natural polymers [143]. Rikhari et al. [144] successfully prepared hydrophilic Ppy coatings on Ti substrates by cyclic voltammetry (CV) and investigated the electrochemical corrosion behavior of Ppy coatings in simulated body fluids (SBFs). Electrochemical testing revealed that the Ti substrate covered with Ppy coating had higher charge transfer resistance (R_t), higher polarization resistance (R_q), and lower corrosion current density (I_{corr}). Khan et al. [145] prepared a polypyrrole coating (PPyNSE) immobilized with bovine serum protein (BSA) and n-succinimidyl ester (NSE) on a steel substrate. This coating was stable, smooth, and had low hemolysis. After 2 h of PPyNSE coincubation with platelet-rich plasma, only a few inactivated platelets were attached to the surface, suggesting that this coating had high resistance to platelet adhesion.

One of the best strategies for improving the biocompatibility of metallic materials involves preparing polymer coatings on metal surfaces. Biodegradable and absorbable polymers can be easily manufactured, and the probability of infection and implant rejection is minimal [146,147]. These polymers can not only improve the biocompatibility of metal surfaces, but also improve the corrosion resistance of metals.

3.2.3. *Drug functional coatings*

3.2.3.1. Heparin coatings. Heparins (Fig. 12 A) are the most widely used polysaccharide anticoagulant drugs in clinical practice [141], with anticoagulant, antithrombotic, anti-inflammatory and lipid-regulating effects, and are mainly used in cardiovascular and cerebrovascular diseases, and hemodialysis treatments [148]. Heparin can be immobilized on material surfaces in different ways to obtain heparinized and functionalized anticoagulant surfaces, effectively reducing blood activation after contact with artificial surfaces [149].

Heparin is a strongly electronegative biomolecule, because it contains abundant negatively charged groups such as $–OSO_3^-$ and $–COO^-$. Immobilization of the heparin molecule on a material surface occurs through the ionic bonding formed by the interaction of positive and negative charges. The ionic bonding immobilized heparin was found to be more stable than physical adsorption, which can maintain the natural conformation of heparin and optimize the anticoagulation effect. However, when only relying on the ionic bonding of heparin on material surfaces, heparin will be easily washed away, especially in complex environments within the human

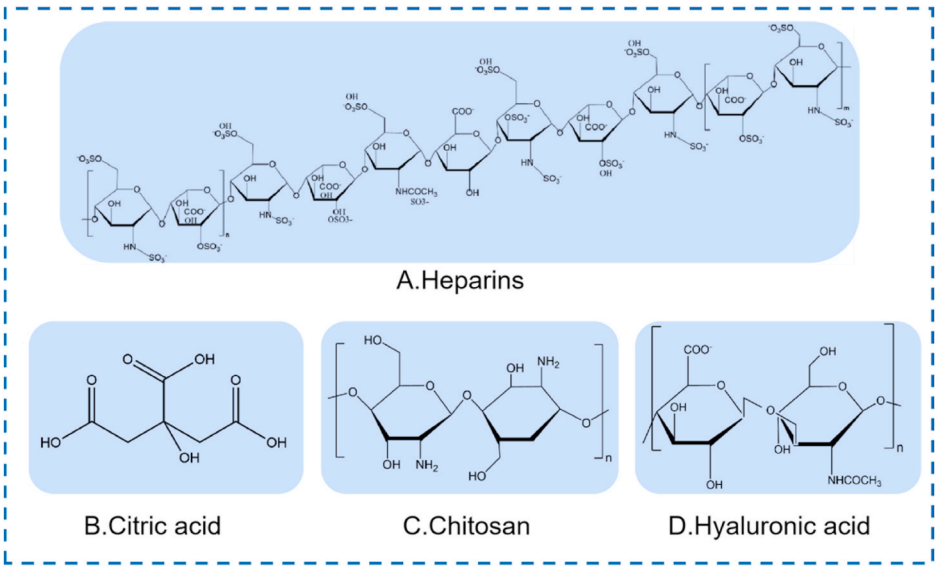


Fig. 12. Pharmaceutical chemical formula: (A) Heparins; (B) Citric acid; (C) Chitosan; (D) Hyaluronic acid.

body. During the washout of blood flow, achieving a long-lasting anticoagulant effect will be difficult. In 1963, Gott et al. [150] found that colloidal graphite surfaces could bind heparin when flushed with a cationic surfactant. Chen et al. [151] modified chain-linked polyurethane with an epoxy monomer and performed a ring-opening reaction with diethanolamine to import numerous hydroxyl groups on the membrane surface, and then grafted cationic monomers on the membrane in the presence of tetravalent cerium salt as an initiator to obtain an anticoagulant coating containing heparin through ionic bonding.

The layer-by-layer (LBL) self-assembly method involved the alternating assembly of heparin molecules and other substances on the substrate surface by electrostatic attractive forces to form highly ordered coatings that possessed multifunctional properties. The coating prepared using this method had a relatively high concentration of heparin molecules, thus, ensuring the anticoagulant properties of the coating. Gao et al. [152] alternately immobilized heparin and chitosan functionalized graphene oxide (GOCS) on magnesium alloys by LBL to fabricate GOCS/Hep bioactive multilayer coatings, which not only endowed the magnesium alloy with excellent corrosion resistance in vitro, but also remarkably reduced the hemolysis rate, platelet adhesion, and activation, as well as enhanced endothelial cell adhesion and proliferation. The mechanism of this coating on corrosion resistance and biocompatibility is shown in Fig. 13.

Heparin molecules can also be immobilized on a material surface through covalent bonds. Heparinized surfaces formed using this strategy are relatively stable and can be exposed to in vivo environments for a long time, with a relatively high heparin utilization rate. However, the covalent bond mode may cause physical damage to the native material and covalent bonds may change the normal conformation of heparin, thus, reducing its anticoagulant activity. Therefore, the covalently bonded heparin material will be less effective in anticoagulation. Zhang et al. [153] immobilized heparin on alkali-treated Ti surfaces, as alkali-treatment can change the topography and chemistry of Ti, resulting in the formation of –OH, which can enable better binding with heparin. Thus covalent immobilization can serve as an efficient and potential solution for titanium surfaces applied in blood-contact medical devices.

Photochemical methods can utilize molecules with photoactive groups to covalently immobilize heparin molecules on the material surface. This method can stabilize the highly ordered heparin on thepolymeric material surfaces, reduce the deposition of proteins and lipids, and enhance the surface activity of biological materials. Li et al. [154] found that immobilizing heparin derivatives containing aryl azide side groups onto polyurethane surfaces using a one-step photo-grafting method effectively inhibited platelet adhesion and prolonged the plasma recalcification time, prothrombin time, thrombin time, and activated the partial thromboplastin time to a significant extent.

Heparin also can be used as a dopant for immobilization on polymers. Liu et al. [155] constructed novel fibronectin-loaded poly-L-lysine/heparin nanoparticles for stent surface modification, and a schematic illustration of the surface modification is shown in Fig. 14. The nanoparticle-modified surface obviously decreased platelet adhesion and activation, and accelerated endothelialization.

3.2.3.2. Citric acid coatings. Citric acid (CA) (Fig. 12B) is a natural weak acid and its sodium salt serves as one of the most prevalent anticoagulant and anti-inflammatory agents. Calcium ions are crucial for prothrombin activation and the coagulation process. Citric

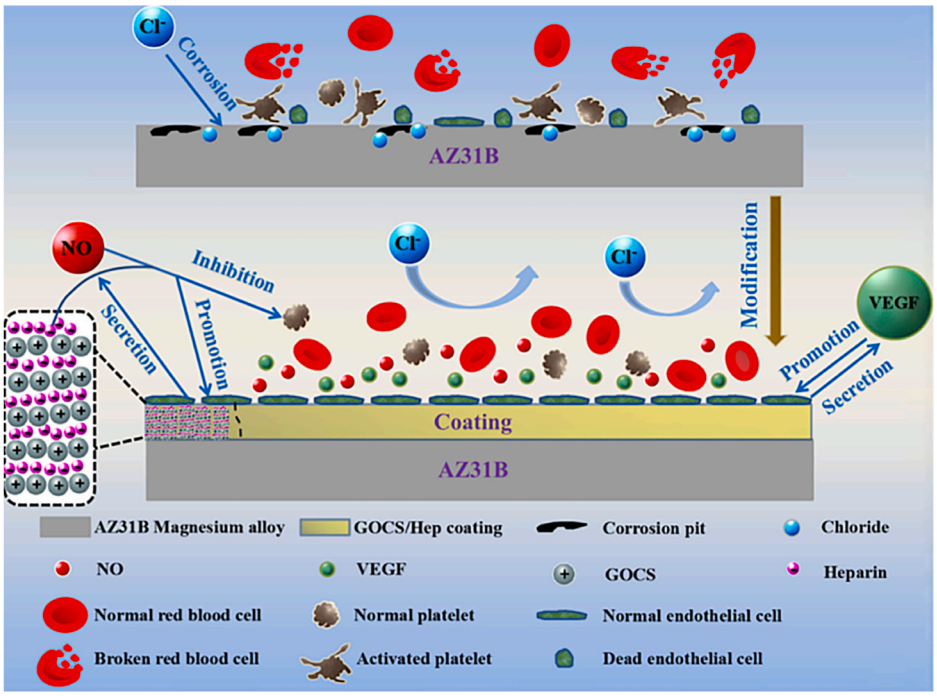


Fig. 13. Mechanism of the GOCS/Hep multilayer coating on the corrosion resistance and biocompatibility of a magnesium alloy surface. Reprinted with permission from Ref. [152]. Copyright 2020 KeAi Publishing Communications Ltd.

acid ions can combine with calcium ions to form soluble, non-degradable complexes, thereby reducing the concentration of calcium ions in the blood and acting as inhibitors of coagulation [156]. CA can reduce endothelial dysfunction and inflammation, promote EC sprouting, and stimulate angiogenic factors [157]. Ceresnakova et al. [157] found that a CA-containing coating possessed good anti-inflammatory properties, suppressed the expression of pro-inflammatory cytokines in simulated experiments, and maintained the activity of ECs and SMCs in mice with good biocompatibility. The researchers demonstrated that CA could serve as a potential candidate for use as an endovascular stent coating. Kou et al. [158] obtained the multifunctional coatings of CA and Arg-Gly-Asp (RGD) with excellent endothelialization properties by immobilizing them on a polydopamine (PDA) deposited surface via LBL. The multifunctional coating of PDA/(CA-RGD) achieved significant improvements in corrosion resistance and hemocompatibility. A schematic illustration showing the preparation of PDA/(CA-RGD) coatings and the function of PDA/(CA-RGD) coatings in accelerating endothelialization are shown in Fig. 15a and b, respectively.

3.2.3.3. Chitosan coatings. Chitosan (Fig. 12C) is a linear polysaccharide and deacetylated derivative of chitin, existing in the shell of crustaceans and cell walls of some fungi. As the only natural alkaline polysaccharide with good biocompatibility and biodegradability, chitosan is a promising material for biomedical applications with water solubility, low cytotoxicity [159], antioxidant, and antibacterial properties, good biocompatibility and film-forming ability [160]. Chitosan coatings have often been used to coat biodegradable stents to mitigate their degradation in vivo. Kozina et al. [161] used a spin-coating technique to prepare a uniform chitosan composite coating on the surface of a Mg20Zn alloy, which significantly improved the corrosion performance of the Mg alloy in Hank's solution at 37 °C. The corrosion potential positively shifted, the corrosion current became smaller, and the corrosion rate decreased by 62.5%. Li et al. [162] invented a copper-containing chitosan composite coating that effectively promoted the proliferation of HUVECs. This coating mitigated the corrosion of the magnesium alloy substrate and alleviated the issue of increased pH in body fluids due to magnesium corrosion. D'Almeida et al. [163] covalently prepared chitosan coatings on titanium substrates and observed their excellent antimicrobial activity by measuring the number of colony forming units of Escherichia coli and Staphylococcus aureus. The chitosan coating significantly improved the safety of titanium implants and could serve as a commercially promising approach.

3.2.3.4. Hyaluronic acid coatings. Hyaluronic acid (HA) (Fig. 12D) is a linear non-sulfated anionic polysaccharide that can inhibit platelet adhesion and aggregation. To evaluate its potential as a coating for stents and other cardiovascular devices, Stefan et al. [164] covalently bonded HA onto the surface of 316L stainless steel tubing. Using a baboon thrombosis model to measure platelet accumulation and following observation with a gamma scintillation camera, the researchers found that the HA coating reduced platelet deposition to 94%. After exposure to blood, the control stainless steel tube contained a significant number of adhered erythrocytes, leukocytes, platelets, and fibrin, while the coated sample had a smooth surface with only a few erythrocytes and leukocytes in the stent convergence area. Li et al. [165] prepared a composite coating consisting of HA and type IV collagen (CoIV) on a titanium substrate. The whole blood assay results obtained under bionic flow indicated that the HA coating effectively inhibited inflammatory response by significantly reducing the activated adhesion of fibers, erythrocytes, platelets, and macrophages. The control samples without HA all showed enhanced serious platelet aggregation of deformation as well as the appearance of visible pseudopods. To fully explore the in vivo safety of the HA coating, the researchers implanted samples into rats for 3 weeks after subcutaneous implantation and found that the HA/CoIV samples exhibited better histocompatibility with weaker tissue reactions, less granulation tissue, and thinner fibrous envelopes. Jiang et al. [166] prepared HA nanoparticle composite films (HA-NCFs) on 316 stainless steel and fully demonstrated their biocompatibility and time-dependence for application as vascular stents. According to Fig. 16A, the surface was shown to inhibit the adhesion and agglomeration of platelets. The inhibitory effects of the surface on platelet coverage, platelet activation, and fibrinogen adhesion are demonstrated in Fig. 16(B–D). Initially implanted in vivo, the HA-NCFs showed a slight inhibitory effect on HUVECs. After 1 day, the researchers observed enhanced adhesion and proliferation of ECs, which supported rapid endothelialization within 1 month of vascular stent implantation in vivo. The HA-NCFs notably inhibited the adhesion and proliferation of human umbilical artery SMCs, avoiding endothelial proliferation and restenosis. In addition, the HA-NCFs exhibited antibacterial ability by inhibiting

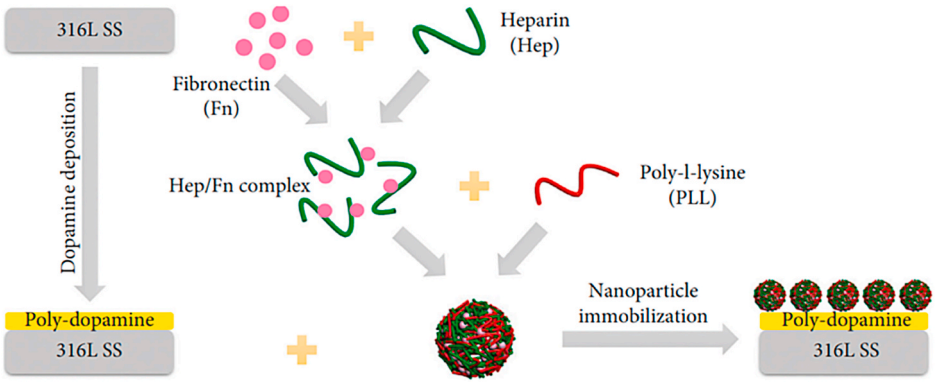


Fig. 14. Schematic diagram of fibronectin-loaded nanoparticle preparation and fixation. Reprinted with permission from Ref. [155]. Copyright 2019 Hindawi Publishing Corporation.

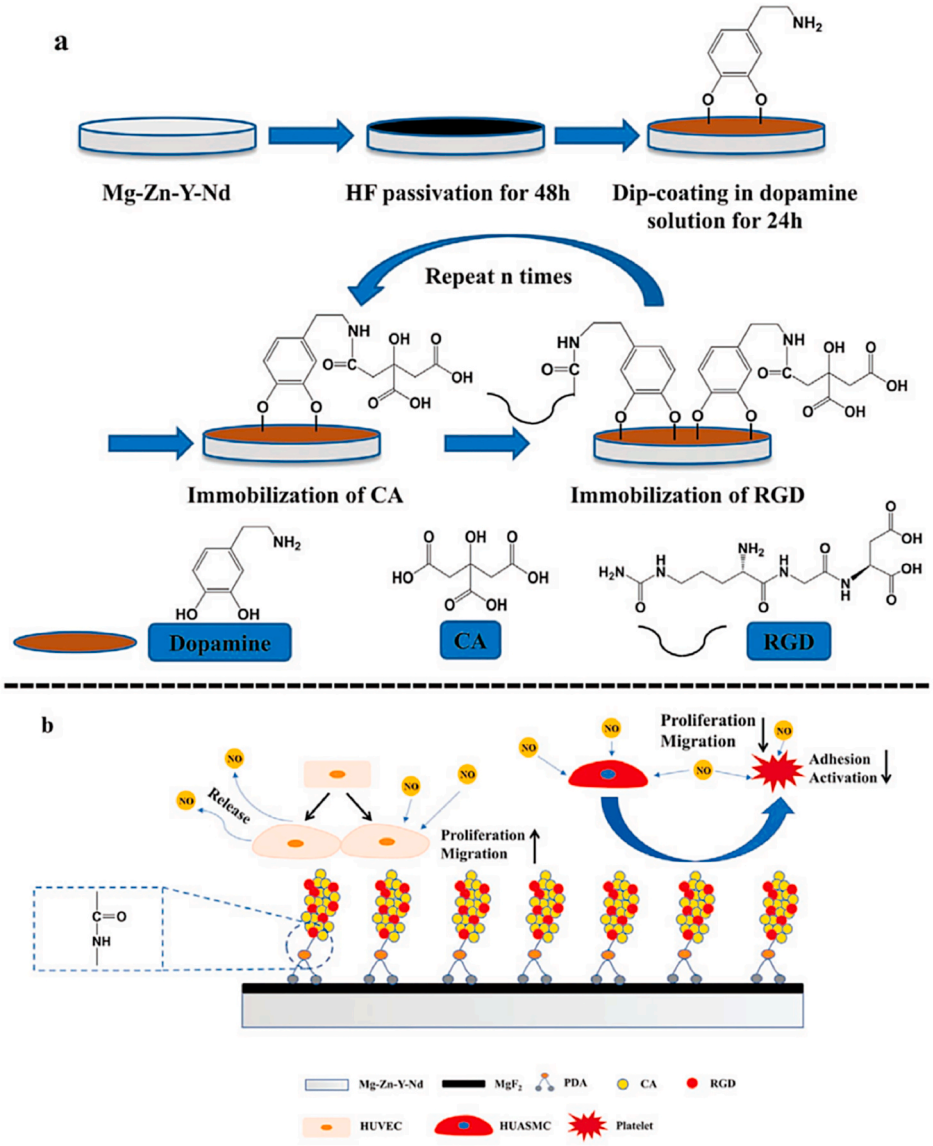


Fig. 15. (a) Schematic showing the fabrication of PDA/(CA-RGD) coatings on the surface of Mg–Zn–Y-Nd and (b) schematic diagram to illustrate the function of PDA/(CA-RGD) coatings in promoting endothelialization. Reprinted with permission from Ref. [158]. Copyright 2021 John Wiley and Sons.

pseudomonas aeruginosa and staphylococcus aureus, thus, achieving the sustained biocompatibility requirements for vascular stent design.

3.2.4. Biofunctional coatings

The immobilization of bioactive molecules on the material surfaces to prepare biofunctional coatings can effectively regulate the behavior of ECs, which may serve as an effective strategy for improving biocompatibility and endowing biomaterials with new bioactive properties.

Studies have shown that administering the vascular endothelial growth factor (VEGF) or stromal cell-derived factor-1α (SDF-1α) can have a therapeutic effect on promoting angiogenesis during wound healing [167]. Liu et al. [168] prepared a coating (NPLS) containing adhesive protein and SDF-1α on 316 SS, achieving accelerated endothelial regeneration by inducing endothelial cell migration and endothelial progenitor cell (EPC) aggregation through SDF-1α release. The experimental results indicated that this new coating greatly promoted the release of single cell NO, as well as the secretion of PGI2 and VEGF. The single-layer ECs that adhered to the NPLS surface diffused to over 90% of the surface on the third day, exhibiting a normal growth morphology. After co-culturing EPC with samples in a microporous cross pore culture dish, more cells migrated through the semi permeable membrane during NPLS incubation. A cell adhesion ability test under fluid conditions confirmed that the incorporation of laminin could enhance the adhesion

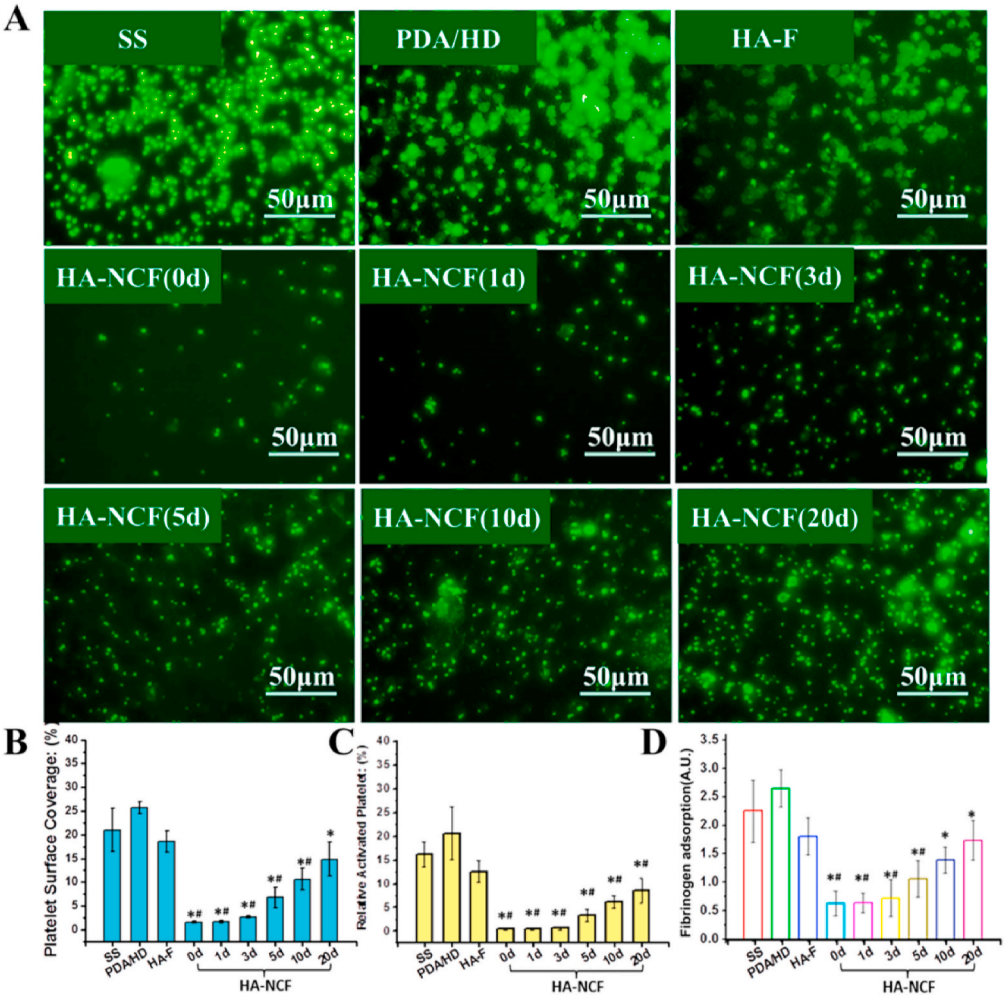


Fig. 16. (A) Rhodamine fluorescence staining of platelets on samples, (B) platelet surface coverage, (C) relative platelet activation, and (D) fibrinogen adsorption on different surfaces. Reprinted with permission from Ref. [166]. Copyright 2019 American Chemical Society.

strength of cells. Wang et al. [169] applied mussel adhesion protein (MAP) as a coating on a 316L stainless steel substrate, and subsequently immobilized VEGF and CD34 antibodies as representative biomolecules onto this coating (CD34 is a highly glycosylated type I transmembrane protein that plays an important role in mediating cell adhesion). The coating showed good cytocompatibility with a hemolysis rate well within 1% and a relative growth rate (RGR) of more than 99%.

Exosomes are typically released into the extracellular space and transport lipids, mRNA, and proteins into target cells to alter cellular behavior. Hou et al. [170] used natural nanoparticle exosomes to modify degradable Mg–Zn–Y-Nd alloys. The adhesion of exosomes was found to improve VECs, proliferation, and nitric oxide (NO) release, which could accelerate surface endothelialization. In addition, the morphology of coated platelets was observed by scanning electron microscopy, which demonstrated that the presence of exosomes not only effectively avoided platelet activation deformation, but also reduced the platelet coverage area from 13% to 8%.

TNF-α is a major inflammatory factor secreted by macrophages that can label classically activated macrophages (M1), with anti-inflammatory functionality. Increased TNF-α is considered to be closely associated with apoptosis, delayed endothelial regeneration, and smooth muscle proliferation in ECs during stent implantation. CD206 was used to label non-activated macrophages (M2), possessing pro-endothelialization functionality. Macrophages co-cultured with exosome-containing samples expressed lower TNF-α and higher CD206 within 3 days, as detected by flow cytometry, suggesting that the novel coating had anti-inflammatory functionality and pro-endothelialization potential for macrophages. Furthermore, the exosome-containing coating not only had a low hemolysis rate, but also low fibrinogen adhesion to deformation on its surface, which provided better biosafety. Cui et al. [171] immobilized albumin and catalase on the surface of TiO_2. The tight immobilization of catalase on this surface and the selective adsorption of albumin on the UV-treated surface made it difficult to displace fibrinogen (FGN). The adsorption and denaturing behavior of the FGN was decisive for the formation of thrombus on the surface of the material. The enzyme-linked immuno-assay (ELISA) results showed that the TiO_2 containing this novel biofunctional coating demonstrated the lowest exposure to the FGN γ chain, which was an important trigger for coagulation. IL-10 is one of the main anti-inflammatory cytokines secreted by macrophages and helps to repair normal tissues on the

stent surfaces. Hydrogen peroxide can promote the secretion of TNF-α by macrophages and inhibit the secretion of IL-10 in macrophages. Due to the peroxidase in the coating, which broke down hydrogen peroxide from the macrophages, the samples had a low expression of TNF-α and high expression of IL-10. This coating inhibited fibrinogen-platelet-mediated coagulation, suppressed the proliferation of SMCs, and protected ECs from free radical damage, offering new ideas for increasing the biofunctionality of cardiovascular stents and improving biocompatibility.

4. Conclusions and outlook

The medical metal materials and surface modification methods reported in this review offer significant potential for the treatment of cardiovascular diseases. However, all of the compositions, structures, shapes, and released substances in the implanted materials may have different negative effects on the human body, and contain a variety of idiosyncratic reactions, as well as inflammation and allergy effects. Therefore, considering human safety, good biomaterials must have superior comprehensive performance and extensive comprehensive tests must be carried out before practical application. Until now, research on new stents has remained insufficient, and the long-term effects of implantation remain unclear. Therefore, more systematic experimental systems are needed for the research of vascular stents, requiring an enormous workload, abundant experimental equipment and a detailed performance testing process (including blood compatibility test, cytotoxicity, releasable material detection, and mechanical strength). Few in vivo animal experiments have been conducted, which is a crucial and essential step for the future of materials for therapeutic applications. In vivo experiments require the long-term tracking of changes and whether the body will experience adverse reactions. To improve the performance of cardiovascular stents employing coating methods, more studies on certain important properties need to be conducted, such as coating bonding, durability, and resistance to blood washing.

For the further application of cardiovascular stents in practical applications, we propose the following three key research directions.

(1) Improving stability and durability is the most critical direction for developing cardiovascular stents. Cardiovascular stents are implanted into the human body through interventional procedures, and require high precision, technology, and safety. The most fundamental performance of cardiovascular stents is stability. However, current research on the stability and durability of stent surfaces is still lacking. Most applied stents are permanent, and their stability and durability must be further improved. If the stent lacks a stable surface, the attack of elements in the body can cause the positively charged ions in the stent to enter the surrounding tissues, subsequently accelerating the inflammatory process. The mechanical properties of stents are also important factors, and poor biomechanical stability of the allografts can induce aneurysms, directly leading to the failure of the implant. For resorbable stents, stability is also important. For example, magnesium alloy stents, as bioresorbable materials, have localized corrosion, which may lead to undesirable results in terms of stress concentrations and early loosening of the implant before adequate tissue reconstruction. Researchers have improved the durability of metal stents by improving mechanical stability, chemical stability, and functional stability. First, materials must be selected with certain mechanical strength and low yield strength, and then the surface must be passivated or a coating prepared to isolate the substrate material and body fluid. Finally, the stability of coatings can be strengthened or drugs can be exerted on the surface to improve the anticoagulant properties.

(2) The stent preparation process must be simplified the cost of stents needs to be reduced. Although the price of stents has significantly decreased, with the advancement in technology, the preparation of new multifunctional stents remains cumbersome and expensive. For example, drug-eluting stents are safe and effective in avoiding postoperative restenosis, however, they are relatively expensive and many drugs are limited to single-use [172]. Therefore, the financial pressure of cardiovascular stent implantation is still prohibitive for the average family. It may be possible to simplify the preparation of the vascular stent substrate skeleton by direct injection molding or 3D printing technology, and a one-step electrodeposition method may be used to simplify the process of preparing the coatings.

(3) Biodegradable stents need to be prepared. An ideal biodegradable stent should safely degrade in the body after functioning, effectively avoiding the permanent negative effects of conventional stents implanted in the body. At present, matrix materials that are bio-absorbable are composed of iron [173,174], magnesium [45,46], and zinc alloys [49,65], and bio-absorbable polymer coatings contain polyesters [175], polyurethanes [176], polydopamine [177], and poly-L-lactic acid [178,179].

Researchers in the field of biodegradable stents should focus on the following two key issues: controlling the degradation rate and accelerating endothelialization. The corrosion rate of metal substrates should be controlled at less than 0.02 mm/year [66]. Effective ways include the surface treatments and coating methods mentioned above, however, comprehensive performance still requires further improvement. To accelerate endothelialization, drug coatings and vascular endothelial growth factors (VEGFs) can be utilized on the stent surfaces. Furthermore, a suitable surface treatment method can be used to obtain vascular SMCs that mimetic surface patterns.

(4) Available feedback must be established. Feedback-enabled stents allow patients to monitor the status of the stent after surgery, maintain long-term patency to avoid the subsequent complications of cardiovascular stent implantation, and provide early warning of thrombosis or restenosis. Intravascular stents can be monitored by magnetic resonance (MR) imaging using weakly magnetic or non-magnetic materials. Superparamagnetic iron oxide nanoparticles can be added to the stent coatings to increase MR imaging capability. In addition, adding prothrombin concentration or fibrin concentration sensors to the stent and setting up an in-stent micro-detection system may achieve the goal of establishing feedback.

Data availability statement

Question	Response
Data Availability Sharing research data helps other researchers evaluate your findings, build on your work and to increase trust in your article. We encourage all our authors to make as much of their data publicly available as reasonably possible. Please note that your response to the following questions regarding the public data availability and the reasons for potentially not making data available will be available alongside your article upon publication. Has data associated with your study been deposited into a publicly available repository?	No
Please select why. Please note that this statement will be available alongside your article upon publication. as follow-up to "**Data Availability** Sharing research data helps other researchers evaluate your findings, build on your work and to increase trust in your article. We encourage all our authors to make as much of their data publicly available as reasonably possible. Please note that your response to the following questions regarding the public data availability and the reasons for potentially not making data available will be available alongside your article upon publication. Has data associated with your study been deposited into a publicly available repository? "	No data was used for the research described in the article

CRediT authorship contribution statement

Xuejia Duan: Writing – review & editing, Writing – original draft, Conceptualization. **Yumeng Yang:** Writing – review & editing, Supervision. **Tianji Zhang:** Supervision. **Benfeng Zhu:** Supervision. **Guoying Wei:** Supervision. **Hongmei Li:** Supervision.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

The authors wish to acknowledge financial support from the National Key R&D Program of China (2021YFC2103100), the National Natural Science Foundation of China (Project 52001300, 52171083), the Fundamental Research Funds for the Provincial Universities of Zhejiang (2023YW05), and the Major Program of Natural Science Foundation of Zhejiang Province (LD24E010003). We thank LetPub (www.letpub.com) for its linguistic assistance during the preparation of this manuscript.

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